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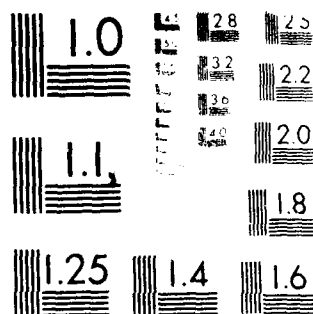
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BASIC STUDY OF FUEL STORAGE STABILITY


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I INTRODUCTION

The objectives of this work were to determine (1) the mechanism by which gum and deposits are formed in diesel fuels, and (2) how to predict and prevent their formation. A parallel research contract on jet turbine fuels of similar properties was supported by NASA-Lewis Research Laboratory. This report describes the principal results of the two programs, for which the results were reported in separate interim reports. The Summary that follows is an expansion of a paper presented to the ARO Engine/Fuels Workshop in Philadelphia on March 27-28, 1984: "The Mechanism of Gum and Deposit Formation from Diesel and Jet Turbine Fuels," by Frank R. Mayo and Bosco Y. Lan.

II SUMMARY OF PRINCIPAL RESULTS

The goal of this program was to determine the chemistry of deposit formation on hot parts of diesel and jet turbine engines and thus to predict and prevent deposit formation. These deposits are assumed to come mostly from soluble gum formed on storage. The fuels used for the study were distilled at low pressure and stored under nitrogen and refrigeration. We measured rates of oxygen absorption from air, R_o , and total gum formation, R_g , at 130°C without initiator and at 100° with added $t\text{-Bu}_2\text{O}_2$. The gum measured was mostly or wholly soluble in the fuel; insoluble gum, if any, was a minor product.

We found no evidence of surface effects with distilled fuels in Pyrex. Table 1 lists the fuels tested at 130° and their abbreviations. The fuels are listed in order of decreasing rates of oxidation (R_o), decreasing rates of gum formation (R_g), and decreasing ratios, R_o/R_g . These ratios measure the oxygen required to produce a milligram of gum. NMP and IND were found to copolymerize so rapidly with oxygen to give polyperoxides that they are not considered further here. The pure hydrocarbons usually oxidize faster than the fuels and have much higher R_o/R_g ratios. To a first approximation, the substrates that oxidize fastest also produce gum the fastest, but the changes in order in the R_g column are of special interest. Although there are few fuels in the upper group of fast-oxidizing substrates, there are several among the fast gum formers. The largest numbers in the last column are associated with low yields of gum for the oxygen absorbed. EtN, the fastest oxidizing of the pure hydrocarbons considered here, is also the outstanding gum former and has the lowest R_o/R_g ratio of all the pure hydrocarbons tested. Table 2 shows that the unstable fuels have the highest contents of condensed aromatic hydrocarbons (e.g., EtN, not alkylbenzenes), as determined by field ionization mass spectroscopy. Except for unsaturates, such hydrocarbons appear to be the main source of instability of fuels.

Table 1

RATES OF OXIDATION (R_o) AND GUM FORMATION (R_g)
AND R_o/R_g AT 130°C

Fuel	R_o ,	R_g ,		R_o/R_g	
	$\frac{\mu \text{ mole } O_2}{g \text{ fuel} \cdot h}$	$\frac{Mg \text{ gum}}{100 g \text{ fuel} \cdot h}$		$\frac{100 \mu \text{ mole } O_2}{mg \text{ gum}}$	
N-Methylpyrrole (NMP)	97	IND	1300	IND	~ 0.07
Indene (IND)	91	NMP	700	NMP	~ 0.13
2-Ethyl-naphthalene (EtN)	89	EtN	68	D	259
Tetralin (TET)	79	B	13	lPH	40
Fuel D (90/10 DOD/TET)	48	PCH	5.7	TET	20
1-Phenylhexane (lPH)	28	C	5.1	Dod	15
Phenylcyclohexane (PCH)	27	TET	4.0	PCH	4.8
n-Dodecane (DOD)	24	BCH	3.9	BCH	4.7
Fuel B (jet)	22	Dod	1.6	B	1.7
Bicyclohexyl (BCH)	19	lPH	0.71	EtN	1.3
Fuel C (jet)	3.8	14	0.58	14	1.3
Fuel 14	0.78	13	0.48	A	0.80
Fuel 13	0.20	15	0.28	C	0.75
Fuel 15 diesel	0.17	1	0.19	10	0.65
Fuel 10	0.09	D	0.19	15	0.59
Fuel 1	0.06	10	0.14	13	0.42
Fuel A (jet)	0.05	a	0.05	1	0.34

Table 2

FUEL COMPONENTS IN ORDER OF DECREASING IMPORTANCE

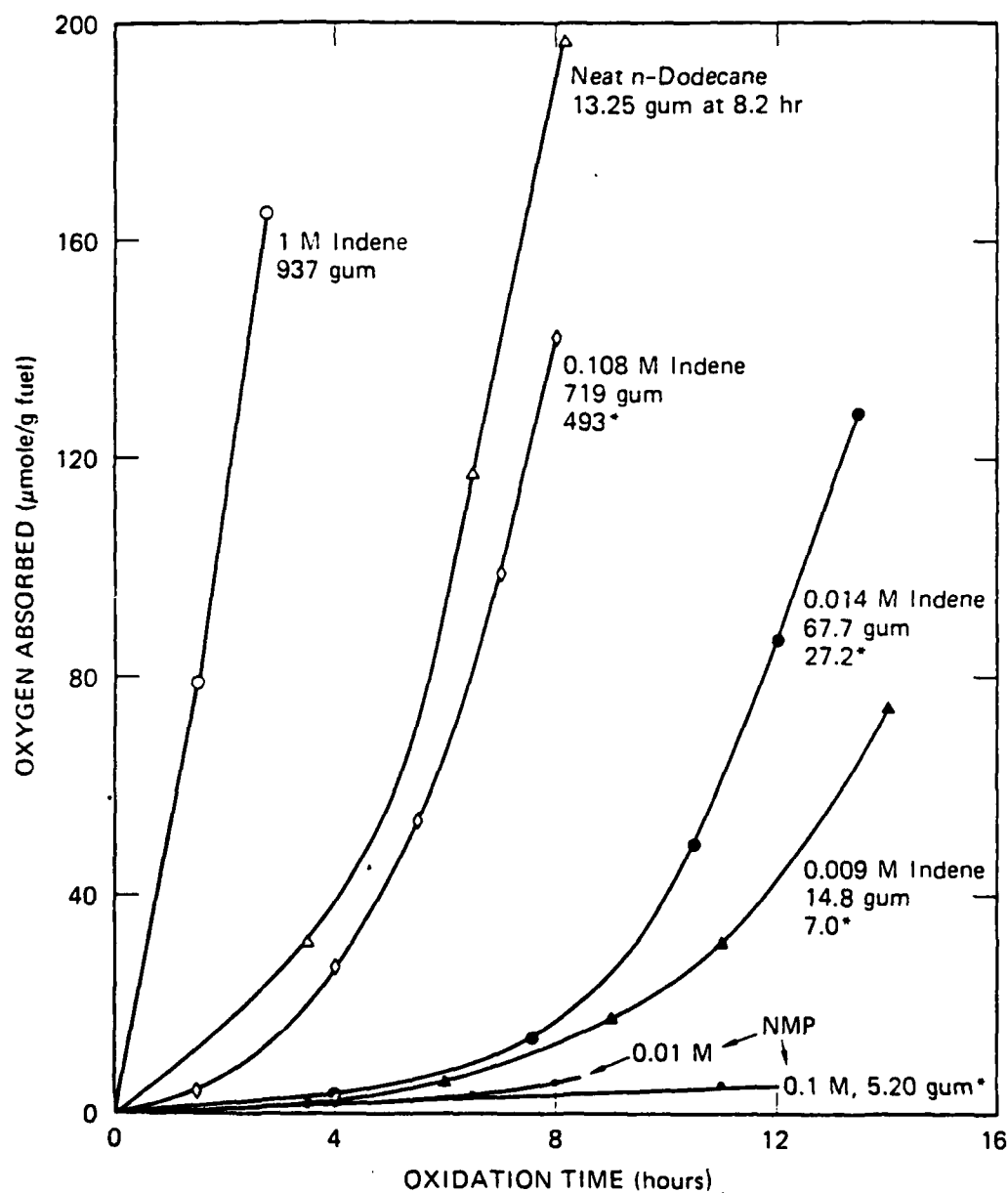
<u>Stable Fuel A</u>	<u>Intermediate B</u>	<u>Unstable Fuel C</u>
Cycloalkanes	Alkylbenzenes	Alkyl-naphthalenes
Bicycloalkanes	Cycloalkanes	Alkylbenzenes
Alkylbenzenes	Alkyl-naphthalenes	Indanes, tetralins
Paraffins	Bicycloalkanes	Acenaphthenes
	Paraffins	Paraffins
	Indanes, tetralins	

We have examined the cooxidations of several mixtures. Figure 1 shows how a small proportion of a very reactive component, indene, may increase R_g , and either increase or decrease R_o of a dodecane mixture, depending on the indene concentration. The reactive component is consumed rapidly. There is no evidence of a catalytic effect of an additive on R_o or R_g .

Table 3 presents similar R_o and R_g data for oxidations with ~ 0.04 M $t\text{-Bu}_2\text{O}_2$ at 100°C . Comparison of Tables 1 and 3 shows that $t\text{-Bu}_2\text{O}_2$ decreases the spread between the highest and lowest values of R_o . The substrates that react fastest at 100°C --EtN, TET, Fuels D and B, and DOD--also react fastest at 130°C , but they react faster at 130°C . Thus, self-initiation at 130° is relatively easy. The slowest-oxidizing substrates--Fuels A, 10, 13--are the same at both temperatures, but they react faster at 100°C than at 130°C . Thus, they lack adequate self-initiation or are self-retarding, or both. DOD shows the largest decreases in both R_o and R_g between 130°C and 100°C ; chain initiation is apparently so easy that normal slowing of all reactions dominates. Fuel D, which is 90% DOD, behaves similarly.

Table 4 shows how gum formation occurs by stepwise coupling of precursor oxidation products. With increasing time, R_o and precursors increase exponentially. However, the molecular weights tend to decrease, especially after 430 min, when the solution becomes lighter and a precipitate, presumably higher molecular weight products, forms.

Table 5 shows the dependence of R_o and R_g on the initial concentration of $t\text{-Bu}_2\text{O}_2$. The second column shows the range of peroxide concentrations available and the third column shows the ratios of the highest to the lowest concentrations. The "Ratio" columns give the ratios of the R_o s and R_g s at the highest and lowest peroxide concentrations. The "Order" columns show the kinetic orders of the dependence of the R_o s and R_g s from the relation, R_o ratio or R_g ratio = (concentration ratio)ⁿ. For the most studied oxidations, R_o depends on [initiator]^{1/2} and a bimolecular termination. Fuel D, ethylnaphthalene (a slower oxidizing and slower gum-forming lot than that described in



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FIGURE 1 OXIDATIONS OF n-DODECANE WITH INDENE AND NMP AT 130°C
Gum is in mg/100 g fuel, determined at 100°C except when marked * for 200°C.

Table 3

OXIDATION WITH ~ 0.04 M $t\text{-Bu}_2\text{O}_2$ AT 100°C

<u>Fuel^a</u>	<u>R_O</u>	<u>R_g</u>	<u>R_O/R_g</u>
EtN	36	EtN 19	D 279
TET	29	C 2.2	DOD 71
PCH	7.6	13 1.6	TET 29
D	6.7	PCH 1.3	B 6.7
B	3.6	TET 1.0	PCH 6.0
C	3.2	10 0.57	EtN 1.9
DOD	1.8	B 0.54	C 1.5
10	0.34	A 0.28	A 1.1
A	0.30	DOD 0.06	10 0.6
13	0.28	D 0.024	13 0.12

^aSee Table 1 for fuel name and units for R_O and R_g.

Table 4
OXIDATION OF DISTILLED FUEL C

	Time at 130°C (min)			
	0	255	430	701
O ₂ consumed, mM	0	6.6	13.1	32.2
mM/hour, previous interval		1.5	2.3	4.2
Precursors				
Concentration (ppm)	74	132	2540	2600
\bar{M}_n	435	388	355	318
\bar{M}_w	496	440	419	381

Table 5
KINETIC ORDERS OF R_O AND R_g

Fuel	[t-Bu ₂ O ₂]	Conc.	R _O	Order	R _g	Order
	M	Ratio	Ratio	n	Ratio	n
A	0.0045 to 0.34	75.6	96 1.055	59	0.94	
D	0.043 to 0.348	8.1	2.86	0.51	11.2	1.16
DOD	0.01 to 0.10	10	1.87 (Average) 2.67 (Initial)	0.27 0.43	2.1	0.32
10	0.01 to 0.10	10	10.2	1.01	9.6	0.98
13	0.01 to 0.10	10	4.5	0.65	10.9	1.04
EtN (old)	0.066 to 0.612	9.3	2.97	0.49	4.3	0.65

Tables 1 and 3), and the initial R_0 for dodecane (the rate is autocatalytic) fit the conventional scheme. However, oxidations of Fuels A and 10 are first order in initiator. Such an order corresponds to termination by a retarder, which may be the fuel itself, or an oxidation product. Fuel 13 is intermediate. Most of the R_g s are close to first order in initiator and thus are associated with the rates of initiation and termination, which are equal. Thus, the gum-forming reaction may well be a small portion of the overall chain termination reaction in which chain-carrying radicals couple. The low orders for R_g for DOD and EtN are unreliable; the oxidation of DOD is autocatalytic and that of EtN is self-retarding.

Rates of oxidation at low pressures of oxygen show that oxidation and gum formation cease at 10 to 20 torr of oxygen at 130°C. Thus, fuel storage stability might be greatly improved even by incomplete removal of oxygen.

In considering the relevance of these results for testing and predicting fuel stability, we assume that gum formation requires oxidation and that deposits come mostly from gum formed on storage. These assumptions are based only on oxidations in Pyrex and require confirmation.

Fuel specifications that require low concentrations of unsaturated and condensed aromatic compounds should ensure good fuel stability. Pyrrole derivatives are fast gum formers as long as they last, but saturated nitrogen compounds, as in shale oil, are probably not important in gum formation.

The suitability of a fuel for early use can be determined by a gum test, but the optimum temperature for the test and initiator, if any, remain to be determined. Fuel color and UV absorption might be suitable for a quick test, but research is needed.

The suitability of a fuel for use after long storage can be gauged by how well it meets the recommended specifications. Oxidation and gum tests like those used in this report should also have predictive values,

but the optimum temperature for these tests must still be determined.

If fuel can be stored at low oxygen concentrations (e.g., 5 to 10% of that in air), gum formation should be reduced, perhaps greatly reduced. Breathing of containers should be avoided.

III PUBLICATIONS

Oxidation and Formation of Deposit Precursors in Hydrocarbon Fuels, F. R. Mayo, S. E. Buttrill, Jr., B. Lan, and D. Dulin, Preprints, Division of Fuel Chemistry, 27(2), 76 (1982).

Gum and Deposit Formation from Jet Turbine and Diesel Fuels, F. R. Mayo and B. Y. Lan, Preprints, Division of Fuel Chemistry, 28(4), (1983); Petroleum Division Preprints, 28(5), 1209 (1983).

Oxidation and Gum Formation from Hydrocarbons and Fuels at 130°C, F. R. Mayo, S. E. Buttrill, Jr., B. Y. Lan, G. A. St. John, and D. Dulin, manuscript for Ind. Eng. Chem. in preparation.

IV PARTICIPATING SCIENTIFIC PERSONNEL

The experimental work on this program was started by Mr. David Dulin and completed mostly by Mr. Bosco Y. Lan and Dr. Frank R. Mayo. Dr. S. E. Buttrill, Jr., and Mr. G. A. St. John performed the work on field ionization mass spectrometry.